........FINAL...........

REPORT

By
THE OHIO STATE UNIVERSITY
RESEARCH FOUNDATION

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COLUMBUS, OHIO 43?12

To........DEPARTMENT OF THE NAVY
Office of Naval Research
Contract No. Nonr-495(16)

Project No. NR 017-606

On........λ-RAY SPECTROSCOPY

For the period........1 May 1958 - 31 May 1964

Submitted by........C. H. Shaw and E. L. Jossem

Department of Physics

Date........July 1964

CONTENTS

I. INTRODUCTION

This final report on Contract Nonr-495(16), (NR 017606) provides a general summary of the work carried out under the contract from its inception on 1 May 1958 to its termination on 31 May 1964. The work under the contract has covered several phases of x-ray physics which are discussed briefly below. Detailed technical discussion of material which has not previously been presented in technical reports or published articles appears in the appendices.

II. X-RAY SPECTROSCOPY

This phase of the work has been concerned with the investigation of x-ray emission and absorption spectra and with their interpretation in terms of current theoretical models. It has also included a study of the instrumental problems which affect the interpretation of the x-ray measurements; in particular, the properties of the crystals used in two-crystal spectrometry and the design of spectrometers and their associated detection and power supply systems.

Crystal Diffraction Patterns

At the time of inception of this research the question of the influence of crystal diffraction patterns on the observed x-ray spectra was of special interest and the first study therefore concerned itself with this problem. Studies were undertaken of the details of the (1,+1) and (1,-1) rocking curves of natural and synthetic quartz and of the effects of radiation damage on the x-ray characteristics of these crystals.

It was demonstrated that the characterization of a pair of crystals for use in x-ray spectrometry by the usual method of specifying only two parameters, viz., the half-width of the (1,-1) rocking curve and the percent reflection, is entirely inadequate. What is required is a knowledge of the complete rocking curve with special emphasis on the shape and relative intensity of the tail regions out to perhaps 50 to 150 half-widths.

It also appears, as a result of these studies, that synthetic quartz crystals are potentially as good or, possibly, even better for x-ray spectrometry than natural quartz. This is important information in the light of the difficulty of securing adequately large and perfect natural quartz.

The radiation damage studies indicate that irradiation sufficient to produce marked coloration of the quartz (ca. 5×10^6 r.) produces no observable effect on the x-ray diffraction patterns.

The details of this work on crystals are contained in the M.Sc. thesis of Mr. Paul C. Claspy which constitutes Appendix A of this report.

L Series X-ray Spectra

The metals in the second transition group have become of increasing technical importance because of their special mechanical, thermal, and electrical properties. Previous work in this laboratory had been concerned with the investigation of the L x-ray emission spectrum of zirconium; under this contract the work was extended to include the L absorption spectra of zirconium and the L spectra of the neighboring elements, niobium and molybdenum.

The interpretation of such spectra has conventionally been made in terms of the theoretical one-electron model of a solid. This interpretation has been called more and more into question by recent experimental data and it seems clear that more sophisticated models and interpretations are required to extract from the experimental x-ray data the desired information about the nature of the electronic energy level structure of the solid. Nevertheless, the experimental data are of major importance in two respects. First, they provide the basis required for even an approximate theoretical treatment of the problem, and, second, they provide guidance as to the direction in which more sophisticated theories must move. On the last point in particular it is most helpful to have the kind of data which have been obtained here, viz., on the variations in properties which occur as one progresses from one element to the next in the second transition group.

A discussion of the experimental results which have been obtained so far is given in Appendix B. It is intended to complete this study under other auspices.

Instrumentation

Considerable effort has been expended on the problems of instrumentation in the soft x-ray region. A new two-crystal spectrometer has been designed and constructed and with it its associated detection, data handling, and power supply systems   A discussion of the design considerations involved is given in Appendix C.

III. X-RAY SCATTERING

This phase of the work has been concerned with the determination of the structures of gaseous and condensed phases of matter by x-ray scattering measurements, and has been previously reported in detail in the technical reports listed below.

Technical Report 809-1: "Calculation of the Transmission Factor in X-ray Scattering." M. Sawada and C. H. Shaw. Journal of Applied Physics 29, 1344 (1958).

Technical Report 809-3: "Low Temperature Spontaneous Transformations in Fine Grained Alkali Metals." K. D. Alexopoulos and C. H. Shaw. The Ohio State University Research Foundation, February, 1961.

Technical Report 809-4: "X-ray Investigation of the Characteristic Temperature of Tungsten." K. D. Alexopoulos and C. H. Shaw. The Ohio State University Research Foundation, February, 1961.

IV. PERSONNEL

During the contract period the following persons have been associated with the research in significant positions.

C. H. Shaw, Supervisor (1 June 1958 - 31 May 1960), Co-supervisor (1 June 1960 - 31 May 1964)

E. L. Jossem, Acting Supervisor (1 June 1959 - 31 May 1960), Co-supervisor (1 June 1960 - 31 May 1964)

R. J. Liefeld, Research Assistant (1 July 1959 - 30 September 1959)

P. C. Claspy, Research Assistant (1 July 1958 - 17 June 1961)

D. L. Waldorf, Research Assistant (14 August 1961 - 31 August 1963)

R. E. Johnson, Jr., Research Assistant (1 September 1958 - 30 September 1958)

It is perhaps not inappropriate to remark here that the work of this contract has played a major role in the training of graduate students in the x-ray program at The Ohio State University. This aspect of the activity, while generally passed over without comment, may in the long run conceivably be of as great importance to the increase of scientific knowledge and to the national security as the more easily recognizable technical information which has been obtained.

V. ACKNOWLEDGEMENT

We wish to record our appreciation of the very cordial relations we have had with the personnel of the Office of Naval Research, as well as for the financial support provided by this contract.

Investigator_____   Date_____

Supervisor____ *C H Shaw*   Date *18 Aug 1964*

C. L. Jossem   *23 February 1965*

For The Ohio State University Research Foundation

Executive Director *Robert C. Stephenson* Date *18 August 1964*

3

APPENDIX A

A STUDY OF THE X-RAY REFLECTION CHARACTERISTICS

OF NATURAL AND SYNTHETIC QUARTZ

A Thesis

Presented in Partial Fulfillment of the Requirements
for the Degree Master of Science

by

Paul Clair Claspy, B. S.

The Ohio State University
1960

ACKNOWLEDGEMENTS

This work was accomplished under the supervision of Dr. E. L. Jossem, whose guidance and encouragement throughout the preparation of this thesis are sincerely appreciated. The helpful criticism of the final draft by Dr. C. H. Shaw is also appreciated.

Finally, I would like to thank my wife for her encouragement, and for her patience in typing this thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

One of the major problems in spectroscopy is that of correcting an observed spectrum for distortions introduced by the spectrometer. In order to make such a correction one must have information about the spectral window (i.e., the spectral response function) of the spectrometer. In x-ray spectroscopy in particular, and especially in the wavelength range in which crystals are used as dispersing elements, the correction problem has long been a serious one in high precision work. Recent developments in techniques for correcting x-ray spectra[1] require a much more intimate knowledge of the

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1. J. O. Porteus and L. G. Parratt, Technical Report No. 7 AFOSR TN 59-754, September 1, 1959. This report considers in detail the factors involved in the problem of correcting spectra obtained with a two-crystal x-ray spectrometer and presents a solution which has been optimized with respect to statistical errors, interpolation and cut off errors, and noise. The report also reviews and gives references to older work in the field.

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spectral window, and thus of the crystal diffraction patterns, than has been common in the past. Furthermore, there has been increasing evidence that the diffraction patterns of crystals--even of such stable material as quartz-- deteriorate with time.[2] This thesis reports an investigation the purpose of

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2. The fact that crystal diffraction patterns show secular variations has been known in a qualitative way to workers in the field for many years. However little or no quantitative data on the phenomenon has appeared in the literature. For unpublished data on the phenomenon see R. Kvarda, M. S. thesis, The Ohio State University, 1957, R. J. Liefeld, Ph. D. dissertation, The Ohio State University, 1959, and J. O. Porteus, Ph. D. dissertation, Cornell University, 1958.

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which was to determine in detail the characteristics of the physical diffraction patterns of some quartz crystals, to attempt to establish criteria for crystal selection, and to attempt to gain some insight into the mechanisms involved in the deterioration of the x-ray reflection properties of crystals.

Quartz was chosen for use in this investigation for several reasons. It has been rapidly replacing calcite in precision x-ray spectrometry because it has been shown[3] that one can obtain quartz crystals which exhibit a high

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3. O. Adell, G. Brogren, and L. E. Haeggblom, Arkiv Fysik 7, 197 (1953).

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value of percent reflection as well as a nominal resolving power[4] of

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4. For a discussion of resolving power, as applied to two-crystal spectroscopy, see Appendix I.

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approximately twice that of calcite.

In addition, the availability of synthetic quartz crystals grown under carefully controlled conditions[5] offered the possibility of a reliable and

5. For a discussion of a method of growing synthetic quartz crystals see e.g.,
    A. C. Walker, Ind. Eng. Chem. 46, 1670 (1954).

continuing supply of spectrometer crystals of high quality. Such a supply
would release researchers from dependence on natural sources where finding
a good crystal is at best a matter of chance.

A detailed comparison of the x-ray reflection characteristics of samples
of natural and synthetic quartz was therefore made during this investigation
and the results are reported herein.

The secular changes in the x-ray properties of the crystals, mentioned
earlier, usually involve a broadening of the diffraction patterns in the
central region, an increase in the magnitudes of the tails of the patterns,
and a decrease in the percent reflection. The exact mechanism (or mechanisms)
by which these changes occur is not known, but they possibly involve a com-
bination of surface corrosion and radiation damage. An attempt to assess the
importance of radiation damage in the deterioration process in natural quartz
has also been made and the results are also reported herein.

Succeeding chapters contain, in turn, a description of the experimental
arrangements, a presentation and discussion of the data and results, and a
summary with conclusions.

CHAPTER II

EXPERIMENTAL APPARATUS

We shall be concerned with the spectrometric properties of the analyzing
crystals used in x-ray spectrometers, especially with the widths and shapes
of rocking curves, and with the values of the percent reflection and coeffi-
cient of reflection. In this chapter we consider briefly the experimental
arrangements used to investigate these properties. In particular we will de-
scribe the two-crystal spectrometer, the x-ray source and detection system,
and the gross physical characteristics of the crystals.

The Spectrometer

The basic design features of the two-crystal spectrometer used have been
described elsewhere.[6] However, two modifications have been made to increase

6. C. H. Shaw, N. Spielberg, and J. Soules, Report No. 8, Contract N6 onr-
22521 NR 017 606, The Ohio State University Research Foundation, Columbus,
May 1951.

C. H. Shaw and N. Spielberg, Report No. 3, Contract No. AT (11-1)-191,
The Ohio State University Research Foundation, Columbus, March 1954.

J. Soules, Ph. D. dissertation, The Ohio State University, 1954.

R. J. Liefeld, Ph. D. dissertation, The Ohio State University, 1959.

the precision and ease of data taking.

During the preliminary work for this investigation it was discovered that the repeatability of small angular measurements with the existing micrometer and linkage mechanism for rotating the second crystal axis was not sufficient for this study. Therefore, this assembly was replaced with a precision micrometer[7] which drives the tangent arm directly. This change enabled

7. Boeckeler Instruments Co., Model 4-3L. This micrometer can be read directly to 20 microinches and is guaranteed to be resettable to within 15 microinches.

measurements of rocking curve widths to be made to ±.05 second of arc.

The second modification was the installation of new crystal holders. The new holders were designed to improve the ease and accuracy of making tilt adjustments. With these holders tilt adjustments can be reset to better than ±30 seconds of arc. In addition, the distance a crystal moves off axis when being tilted has been reduced to a negligible amount (e.g., a tilt of 16 minutes of arc--about the maximum tilt ever used--moves the center of the reflecting area only 70 microinches off axis). The holders have been equipped with Seeman wedges which can be used either as scatter shields or as limiting slits.

X-Ray Source and Power Supply

The x-ray source used in this investigation was a Machlett type A-2 diffraction tube having a copper target and an effective focal spot 1 mm square. Power for the tube was obtained from a 50 kv regulated supply which has been described elsewhere.[8] The power supply was originally provided with

8. J. Collenge, M. S. thesis, The Ohio State University, 1951.

stepwise controls for current and voltage, but these have been modified so that both are continuously variable. Provision has also been made for potentiometric monitoring of both voltage and current. During each data run the voltage was kept constant to within ±0.5 per cent and the current to within ±1 per cent.

Detection System

X-ray photons were detected by a xenon- and methane— filled proportional counter[9] the voltage for which was supplied by an Atomic Instruments Co. model

9. Soules, op. cit., p. 59.

326 high-voltage supply. The pulses from the counter were fed to a preamplifier and linear amplifier (Franklin Instruments Co. model 348) having a built-in single channel pulse height discriminator. The discriminator output was then fed to a scaler (Berkley model 2025) which was controlled by an electronic timer (Berkley model 811).

3

Although the detector was designed for work in the vicinity of 5Å, its quantum counting efficiency at 1.537Å is 38 per cent, which proved to be quite acceptable.

The linearity of this system has been examined by Liefeld,[10] who found

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10. Liefeld, op. cit., p. 31.

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that for counting rates up to 150,000 counts per minute the deviations from linearity are random and less than 1 per cent.

The Quartz Crystals

Our choices of the crystal planes and of the wavelength at which data were taken were influenced by two factors. First, the desire to work in air, and second, the desire to measure rocking curve widths to 1 per cent. The desire to work in air requires use of radiation of sufficiently short wavelength (i.e., less than about 2.5Å) that the absorption of x-rays in the air path through the spectrometer does not seriously limit the intensity available at the detector. In addition, the effects of small changes in crystal properties are more pronounced at short wavelengths than at long. On the other hand, the desire to measure rocking curve widths to 1 per cent or better suggests use of as long a wavelength as possible and use of those crystal planes which have the largest grating space, since the angular width of the rocking curves increases with an increase in either of these quantities. In fact, since the precision of angle measurement is about 0.05 second of arc, we should choose our wavelength long enough and the crystal grating space large enough so that the full width at half maximum of the rocking curves is at least about 5 seconds of arc.

For quartz the conditions discussed above are highly restrictive and our choice of Cu Kα radiation and the (10·0) planes is almost the only reasonable one that can be made under the circumstances.

Physical specifications. Both the natural and synthetic crystals used in this investigation were cut from right-handed, single-crystal α quartz. The natural crystals were quartz of Brazilian origin, and the synthetic crystals were grown by Sawyer Research Products, Inc.[11] All the crystals

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11. Sawyer Research Products, Inc., 35400 Lakeland Boulevard, Eastlake, Ohio

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were cut, ground, and polished by the Valpey Crystal Corporation.[12] The

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12. Valpey Crystal Corporation, Holleston, Massachusetts.

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finished size of the crystals was 2"x 1" x 1/4", and the surfaces were polished to a 20 microinch rms finish. The surfaces were made parallel to each other and to the atomic planes to within 2 minutes of arc. Unfortunately, each synthetic crystal has a section of the seed crystal about 1/4 inch wide

4

in the center of the two-inch dimension. In investigating these crystals, therefore, each synthetic crystal plate has been treated as consisting of three separate single crystals.

Alignment of spectrometer and crystals. Before taking rocking curves it is necessary to have the spectrometer in proper alignment. This includes having the two spindle axes parallel, having the crystal planes parallel, and having the crystal faces on the axis of rotation. This alignment was accomplished in the following manner.

Before putting the crystals in place, an optically flat mirror was inserted in each crystal holder and, with this mirror as one mirror of a Michelson interferometer and using white light fringes, the holders were aligned so that the screws which determine the location of the reflecting surface defined a plane which is on the axis of rotation within ±1.1μ and parallel to it within ±12 seconds of arc. After placing mirrors in both holders, the two spindle axes were made parallel to each other to within 1/2 minute of arc using a telescope equipped with a Gauss eyepiece. Finally the crystals were inserted in the holders and the atomic planes of the two crystals made parallel to each other using an x-ray method.

The x-ray method makes use of the fact that the width of a (1,-1) curve is a minimum when the atomic planes of the two crystals are parallel in the vertical direction. Because of the time involved only those crystals to be extensively investigated were so adjusted. It was found that for these crystals the atomic planes were parallel to the surfaces within ±2 minutes. For the crystals which were not individually adjusted for tilt it is extimated that the values given in Chapter III for the (1,-1) width and per cent reflection are within 2 per cent of the values for perfect alignment. This estimate is made on the basis of average curves of (1,-1) width and of per cent reflection vs. tilt angle obtained with other crystals.

CHAPTER III

DATA AND RESULTS

In selecting crystals for use in x-ray spectroscopy some criteria for selection must be used. In the past the selection has been done by using as criteria the rocking curve widths and values of per cent reflection. Such comparisons will be made in this chapter. In addition we will look at the shape of the whole curve, with particular emphasis on the tails. The data to be presented and discussed in this chapter include rocking curves and their widths and shapes, and values of the per cent reflection and coefficient of reflection. Data on the one crystal which was subjected to radiation damage will also be presented and discussed.

X-Ray Reflection Characteristics

This section discusses the data on the parallel and anti-parallel rocking curves of the crystals. These curves were taken in the usual way, i.e., by rocking the B crystal, leaving the A crystal stationary. One natural crystal, Y4-F,[13] was arbitrarily chosen and placed in the A-crystal

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13. The crystal designations are as follows. Y and YN indicate natural crystals; YS indicates synthetic crystals. The number following the above designation identifies a particular crystal. The letters B and F indicate the arbitrarily selected back and front faces, respectively. The number following the face designation indicates which section of a synthetic crystal is being discussed. Thus, YS-2-F1 is the designation for the first section of the front face of the synthetic crystal number two.

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position. Then (1,-1) curves were run with each of the remaining natural crystals. The B crystal from the pair with the curve having the lowest tails, Y3-F, was then placed in the A position and (1,-1) curves with some of the remaining crystals were taken. On the basis of the width and shape of these curves (low tails), Y3-F and Y4-F were selected as the best pair. Y4-F was used in the A position for the remainder of the work.

Since recording a (1,-1) curve, complete with its tails, is a time-consuming task, a few crystals were selected for further study. These crystals, when paired with Y4-F, gave values of (1,-1) curve width (w), per cent reflection (P), and coefficient of reflection (R) which covered the range of observed values of these quantities. The crystals were Y3-F, Y2-F, Y2-B, YS-2-F1, YS-2-F3, and YS-3-B3. After their (1,-1) curves and values of w, P, and R were determined, these crystals were etched in 48 per cent hydrofluoric acid for five-second intervals until further etching had no effect on the (1,-1) curves. The above quantities were then remeasured for each crystal, again using Y4-F as the A crystal. The index of asymmetry, defined as the ratio of the half-width at half maximum on the positive side of the (1,-1) peak to the half-width at half maximum on the negative side of the peak, was calculated for each curve.[14]

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14. The notation for the positive and negative sides of the rocking curve peak follows that given by A. H. Compton and S. K. Allison, _X-Rays in Theory and Experiment_, (D. Van Nostrand and Co., New York, 1935), 2nd ed., p. 712.

After these selected crystals were etched and the above data taken, the "best" natural crystal (Y3-F), the "best" synthetic crystal (YS-2-F1), and a crystal with anomalous behavior (YS-3-B3) were selected for still further study. Each of these crystals was in turn paired with Y4-F, and (1,+1) curves of the Cu $K\alpha$ doublet were taken. From these curves the widths of the α_1 and α_2 lines, the indices of asymmetry, the overlap factors,[15] the relative

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15. The overlap factor is defined as the ratio of the minimum ordinate between the α_1 and α_2 peaks to the maximum ordinate of the α_1 line, all multiplied by the ratio of intensity of α_1 to α_2.

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intensities of the peaks, and the peak separations were measured.

The data from the above investigations are presented in Tables I through VIII and representative curves are shown in Figs. 1 - 5. The values of w and P are accurate to about 1 per cent,[16] and the values of R are good to about

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16. Because of the high counting rates near the peaks of the (1,-1) curves it was necessary to make corrections for the estimated 3 to 4 microsecond dead time of the detection system. This correction has been made for the measurements of P, but was found to be negligible for w and R.

As stated previously, tilt adjustments have been made on only a few crystals. Since w and P are dependent on the vertical angle between the atomic planes, the values given for these quantities in Tables I and II may not be the optimum ones. However, since w has its lowest value and P has its highest value when the planes are parallel, the values in Tables I and II are, if anything, less favorable than those which would be obtained if the tilt adjustment had been made.

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3 per cent. The crossover points and ratios of (1,-1) curve ordinates to Lorentzian ordinates are good to about 5 per cent. These data will be discussed in subsequent sections.

Empirical correlations. Previous discussions of crystal properties, as involved in resolving power corrections,[17] have attempted empirical correla-

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17. See, e.g., L. G. Parratt, Rev. Sci. Instr. 6, 387 (1935).

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tions among these properties in order to determine a method of characterizing the reflection properties of crystals. Among these correlations are those relating (1,+1) curve width to (1,-1) curve width, and per cent reflection to (1,-1) curve width. Although, as we shall see later, such correlations have but limited usefulness, it is still instructive to examine them. We shall, therefore, first look at the empirical relations, and later compare our results with the existing theory.

We consider first the correlation of (1,+1) width and (1,-1) width (see Fig. 1). The data represented here are those of this investigation and those of Parratt.[17] It can be seen that the three points observed in this investigation fall quite close to the curve. Parratt has classified crystals into two groups according to their spectrometric perfection. Crystals of Class I give points which fall below the curve and those of Class II give points above the curve. According to this classification of crystals, there are two pairs of crystals of Class I and one pair of Class II. Note that two crystals having nearly the same (1,+1) width have different (1,-1) widths, indicating that use of the correlation of (1,+1) widths to (1,-1) curve widths is not a reliable means of crystal selection. This and the other empirical correlations will be discussed in more detail later in the chapter.

We consider next the correlation between per cent reflection and (1,-1) curve width (see Fig. 2). Although most of the points lie near the curve, indicating a rough correlation between these quantities, there is considerable

TABLE I

PER CENT REFLECTION, COEFFICIENT OF REFLECTION, AND (1,-1) CURVE WIDTH FOR THE NATURAL CRYSTALS BEFORE AND AFTER ETCHING*

B-Crystal	w (sec)	w (XU)	P	R** (radians)	Index of Asymmetry
DEP Theory	4.9	.099	64	1.82×10^{-5}	1.00
Y1-F after	5.03	.102	61.0	1.93	1.11
Y1-B after	5.03	.102	62.0	1.92	.91
Y2-F before	10.7	.237	34.8	----	1.07
after	4.93	.100	57.7	----	.92
Y2-B before	10.7	.237	33.9	----	1.02
after	4.93	.100	60.1	2.02	1.06
Y3-F before	5.20	.105	58.5	----	1.00
after	5.15	.105	60.5	1.93	1.00
YN-1-F Nov.	6.00	.122	51.8	----	1.09
June	5.77	.117	----	----	1.09
YN-1-B Nov.	8.80	.178	41.0	----	.87
June	8.35	.169	----	----	.73
YN-2-F Nov.	6.00	.122	51.0	----	.84
June	5.95	.120	----	----	.87
YN-2-B Nov.	6.67	.135	50.5	----	1.02
June	6.64	.135	----	----	1.01

*In each case the A crystal was Y4-F.

**The values of R given here neglect intensity beyond 40 half-widths, but this is believed to introduce an error of no more than 3 per cent.

8

TABLE II

PER CENT REFLECTION, COEFFICIENT OF REFLECTION, AND (1,-1) CURVE WIDTH FOR THE SYNTHETIC CRYSTALS BEFORE AND AFTER ETCHING*

B-Crystal		w (sec)	w (XU)	P	R** (radians)	Index of Asymmetry
DEP Theory		4.9	.099	64	1.82×10^{-5}	1.00
YS-1-F1		5.16	.105	61.0	----	.94
YS-1-F3		5.06	.103	61.2	----	1.03
YS-1-B1		5.10	.103	60.2	----	.97
YS-1-B3		4.96	.101	61.1	----	.96
YS-2-F1	before	5.18	.105	58.9	1.92	1.01
	after	5.01	.102	62.0	1.93	.96
YS-2-F3	before	5.13	.104	58.2	2.12	1.14
	after	5.03	.102	62.6	1.96	.92
YS-2-B1		5.20	.105	63.0	----	.94
YS-2-B3		5.23	.106	61.4	----	.99
YS-3-F1		5.26	.107	60.1	----	1.05
YS-3-F3		5.10	.103	62.0	----	1.07
YS-3-B1		5.02	.102	61.1	----	.94
YS-3-B3	before	6.62	.134	46.4	2.04	.91
	after	6.75	.137	48.6	2.04	.93

*In each case the A crystal was Y4-F.

**The values of R given here neglect intensity beyond 40 half-widths, but this is believed to introduce an error of no more than 3 per cent.

9

TABLE III

RATIOS OF (1,-1) CURVE ORDINATES TO ORDINATES OF A MATCHED LORENTZIAN
AT 5 AND 35 HALF-WIDTHS FROM THE PEAK, AND CROSSOVER POINTS
FOR (1,-1) CURVE CROSSING MATCHED LORENTZIAN*

Crystal	$(C/L)_5$		$(C/L)_{35}$		Crossover	
	+	-	+	-	+	-
Y1-F after**	.47	.53	.61	.55	140	135
Y2-F before	1.66	1.71	----	----	1.0	1.0
after	.86	.88	----	----	9.75	8.0
Y2-B before	1.64	1.64	----	----	1.2	1.0
after	.62	.75	1.02	1.11	26.2	23.0
Y3-F before	.47	.47	----	----	----	----
after	.39	.44	.41	.44	185	185
YS-2-F1 before	.62	.62	.71	.71	----	----
after	.42	.44	.52	.49	----	----
YS-2-F3 before	.88	.83	.99	.99	----	----
after	.44	.47	.49	.50	----	----
YS-3-B3 before	.34	.34	.34	.35	----	----
after	.31	.34	.28	.37	----	----

*In each case the A crystal was Y4-F. The distances of crossovers from the
peak are measured in terms of the half-width at half maximum of the curve
under consideration.

**"Before" and "after" refer to the etching process.

TABLE IV

CHARACTERISTICS OF THE (1,+1) CURVE
OF THE Cu Kα DOUBLET

Characteristic	B-Crystal*		
	Y3-F	YS-2-F1	YS-3-B3
Overlap Factor	5.2×10^{-2}	5.0×10^{-2}	5.1×10^{-2}
(1,+1) width (sec)			
α_1 line	26.2	25.4	26.2
α_2 line	36.0	35.5	35.9
(1,+1) width (XU)			
α_1 line	.530	.514	.530
α_2 line	.732	.720	.725
Index of Asymmetry			
α_1 line	1.14	1.16	1.19
α_2 line	1.33	1.33	1.33
Ratio of Peak Intensities (α_2/α_1)	.415	.425	.423
Peak Separation			
(sec)	189	188	189
(XU)	3.83	3.81	3.83

*With Y4-F as the A crystal. For the parallel position rocking curve characteristics of these crystals see Tables I and II.

TABLE V

CALCULATED CRYSTAL DIFFRACTION PATTERN WIDTHS
ASSUMING LORENTZIAN SHAPE

Crystal	w* (sec)		Single Crystal Pattern Width (sec)	
	Nov. 1959	June 1960	Nov. 1959	June 1960
Y1-F	5.03	----	2.49	----
Y3-F	5.15	5.00	2.59	----
Y4-F	----	----	2.57	----
YN-1-F	6.00	5.77	3.43	3.20
YN-1-B	8.80	8.35	6.23	5.78
YN-2-F	6.00	5.95	3.43	3.38
YN-2-B	6.67	6.64	4.10	4.07

*Measured (1,-1) width with Y4-F as the A crystal.

12

TABLE VI

CALCULATED (1,-1) WIDTHS ASSUMING LORENTZIAN SHAPE

Crystal	w* Calc. (sec)		w* Exp. (sec)		Per Cent Difference	
	Feb. 1960	June 1960	Feb. 1960	June 1960	Feb. 1960	June 1960
Y1-F	5.08	----	5.08	----	0.0	----
YN-1-F	6.02	5.79	7.22	6.62	-16.6	-12.5
YN-1-B	8.82	8.37	6.28	7.17	+40.5	+16.7
YN-2-F	6.02	5.97	5.70	6.38	+ 5.6	- 6.4
YN-2-B	6.69	6.66	6.17	6.26	+ 8.4	+ 6.4

*With Y3-F as the A crystal.

TABLE VII

ETCH PIT DENSITIES

Crystal	w (sec)	Average Number per cm^{-2}
Y1-F	5.08	2.5×10^5
Y2-F	4.93	30
Y2-B	4.93	30
Y3-F	5.15	5.0
YS-2-F	5.03	7.5
YS-3-B	6.75	2.5

13

TABLE VIII

(1,-1) CURVE CHARACTERISTICS
OF CRYSTAL Y1-F BEFORE AND AFTER IRRADIATION

Characteristic	Before Irr.	After Irr.
(1,-1) width*	5.03 sec	5.06 sec
Per cent Reflection	61.0	61.4
Coefficient of Reflection	1.93×10^{-5}	2.03×10^{-5}
Lorentzian Crossover		
+ side of peak	140 ± 5	142 ± 5
- side of peak	135 ± 5	145 ± 5

*With Y4-F as crystal A.

Fig. 1 - (1,+1) Width vs. (1,-1) Width

P vs. W (1,-1)   λ=1.54 A

+ Synthetic Crystals

∘ Natural Crystals
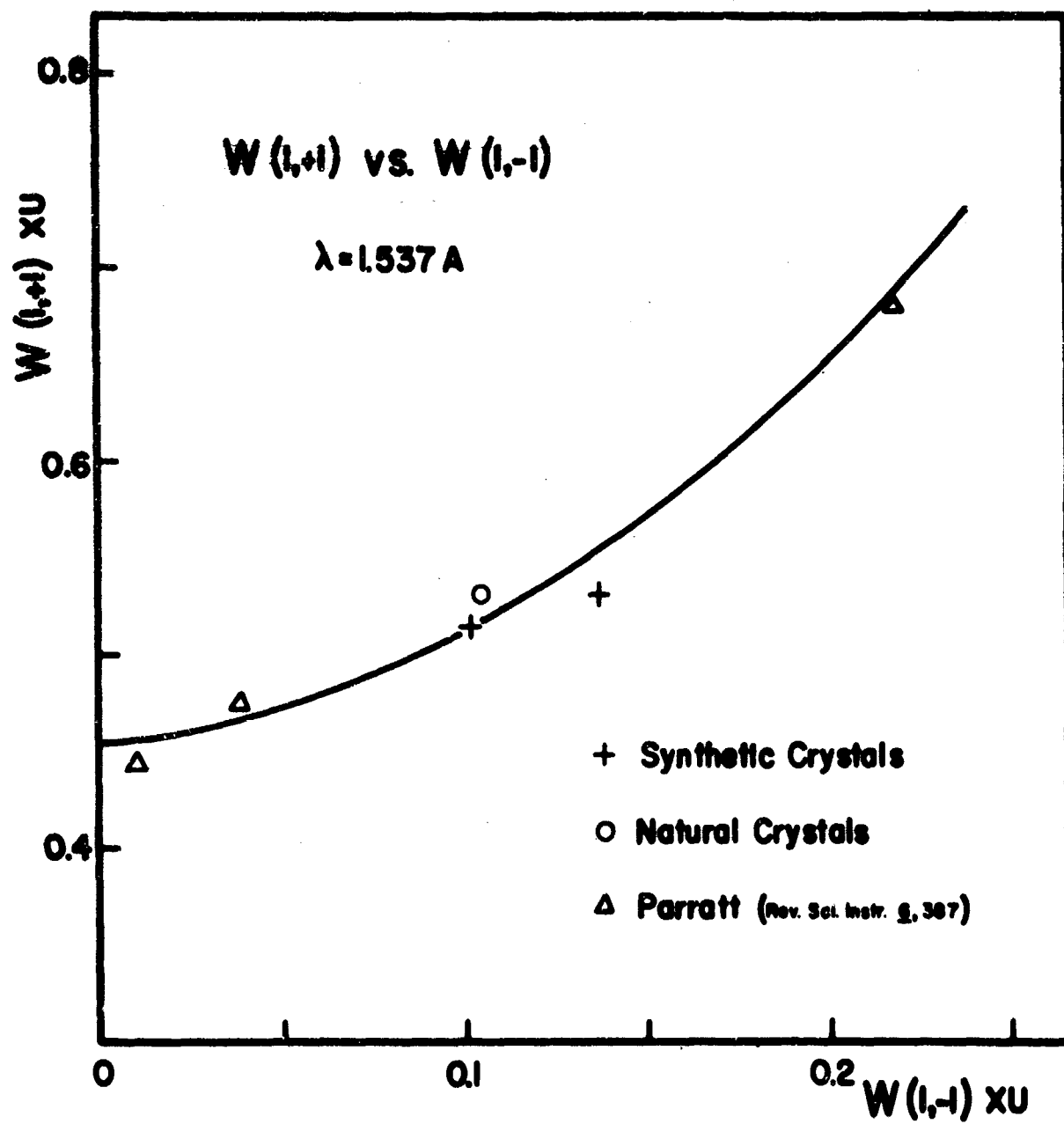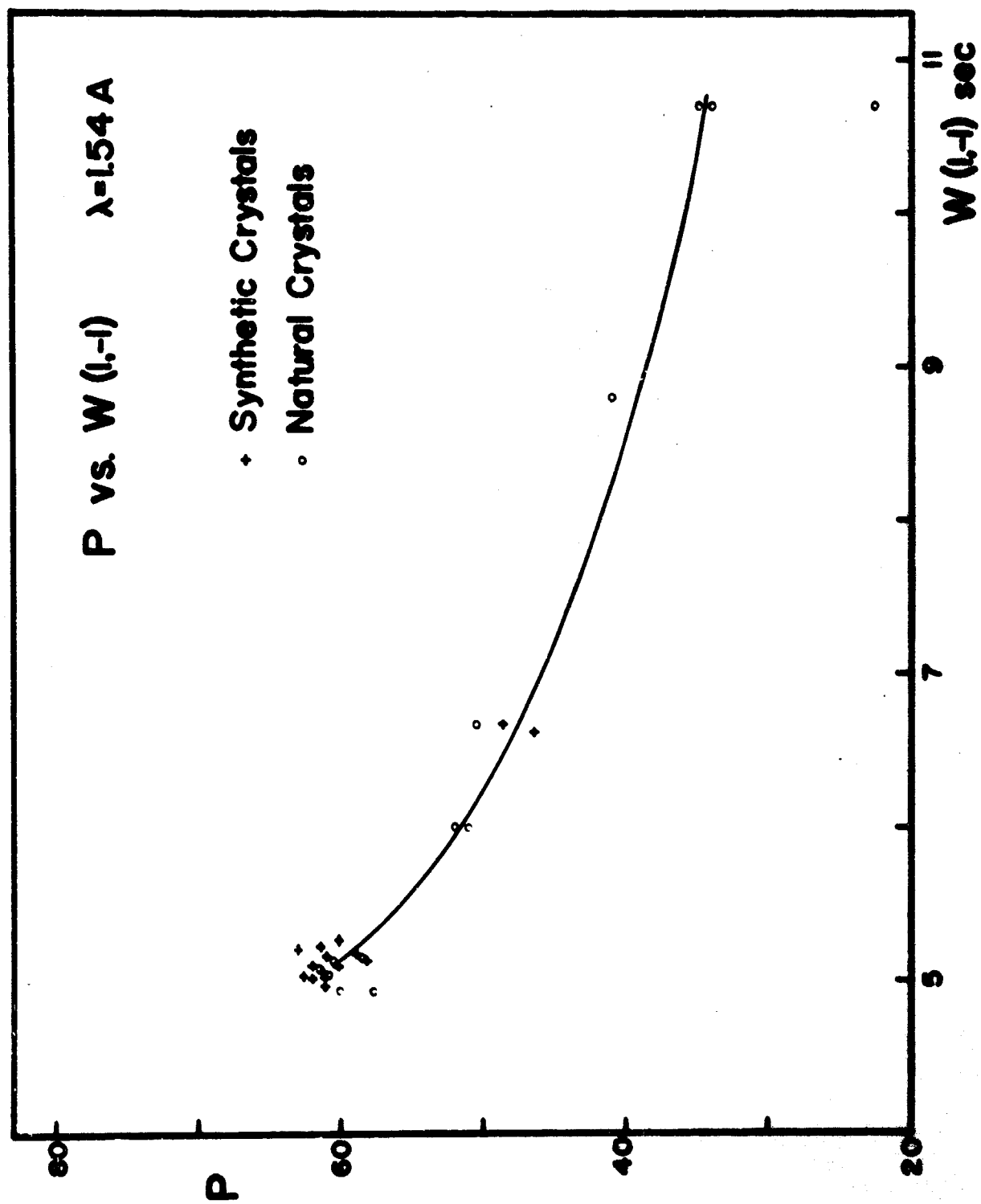
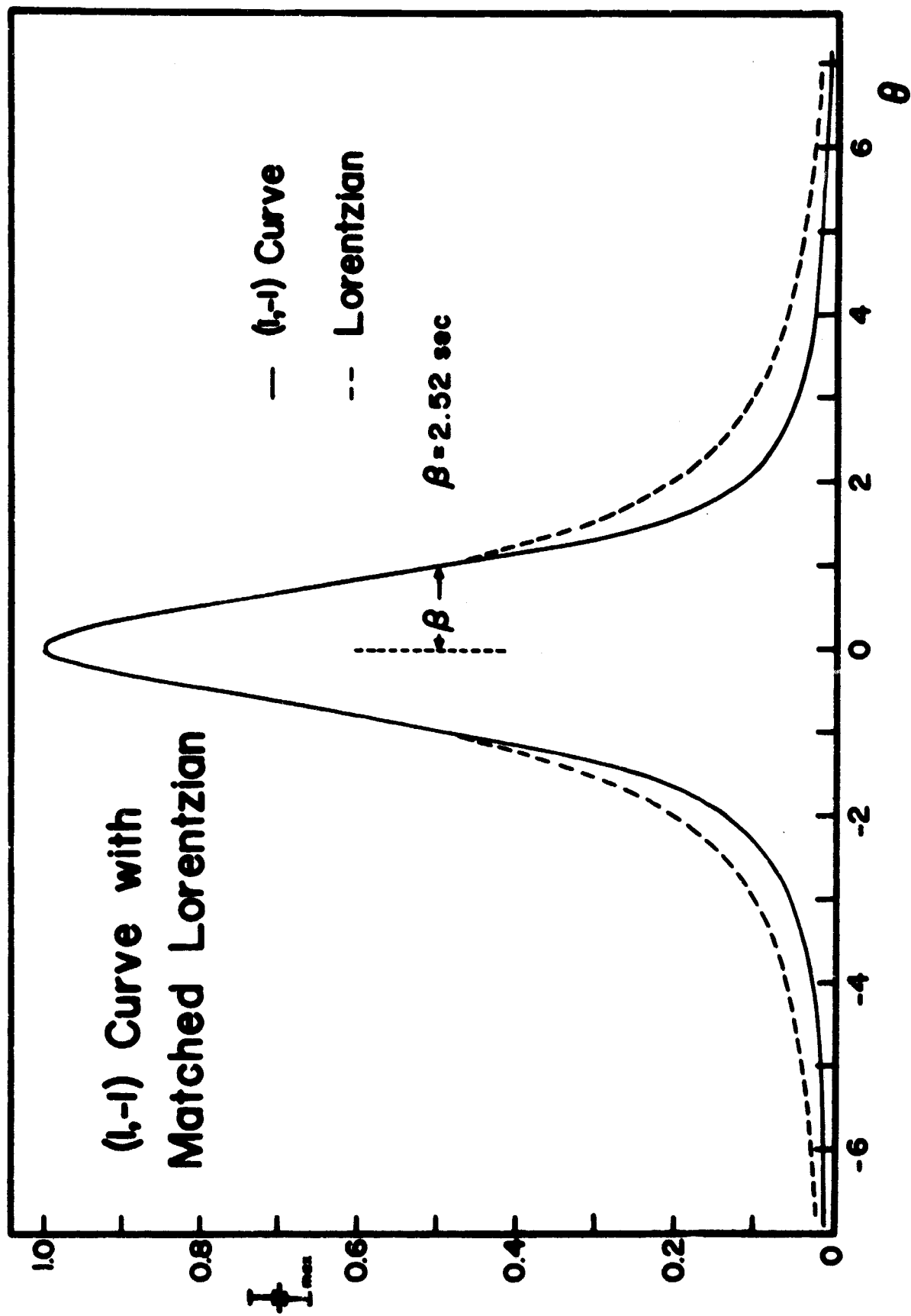Fig. 2 - Percent Reflection vs. (1,-1) Width

Fig. 3 - (1,-1) Curve and Matched Lorentzian for a Typical
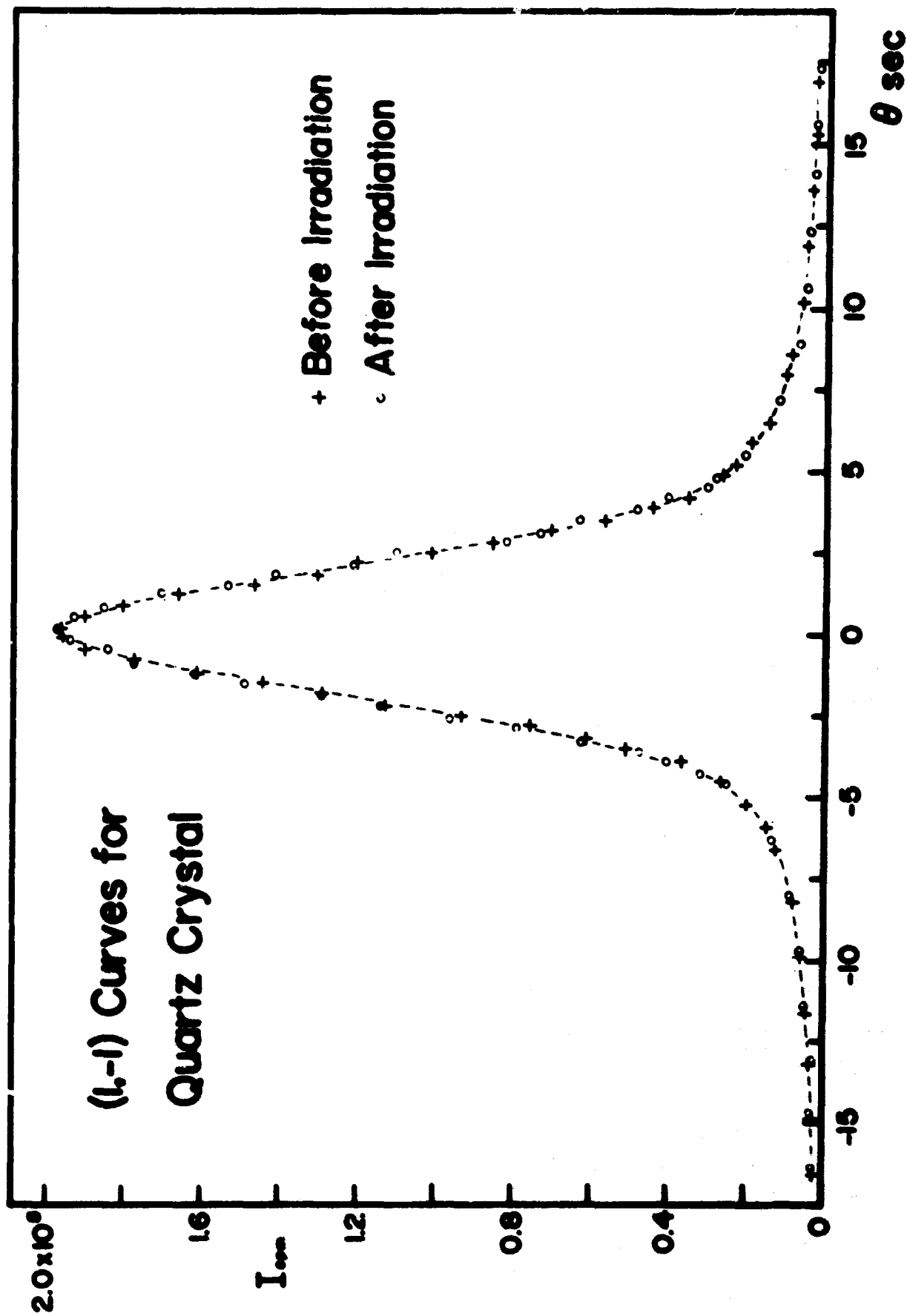Crystal Pair

17

Fig. 4 - (1,-1) Curve of Irradiated Crystal Before and
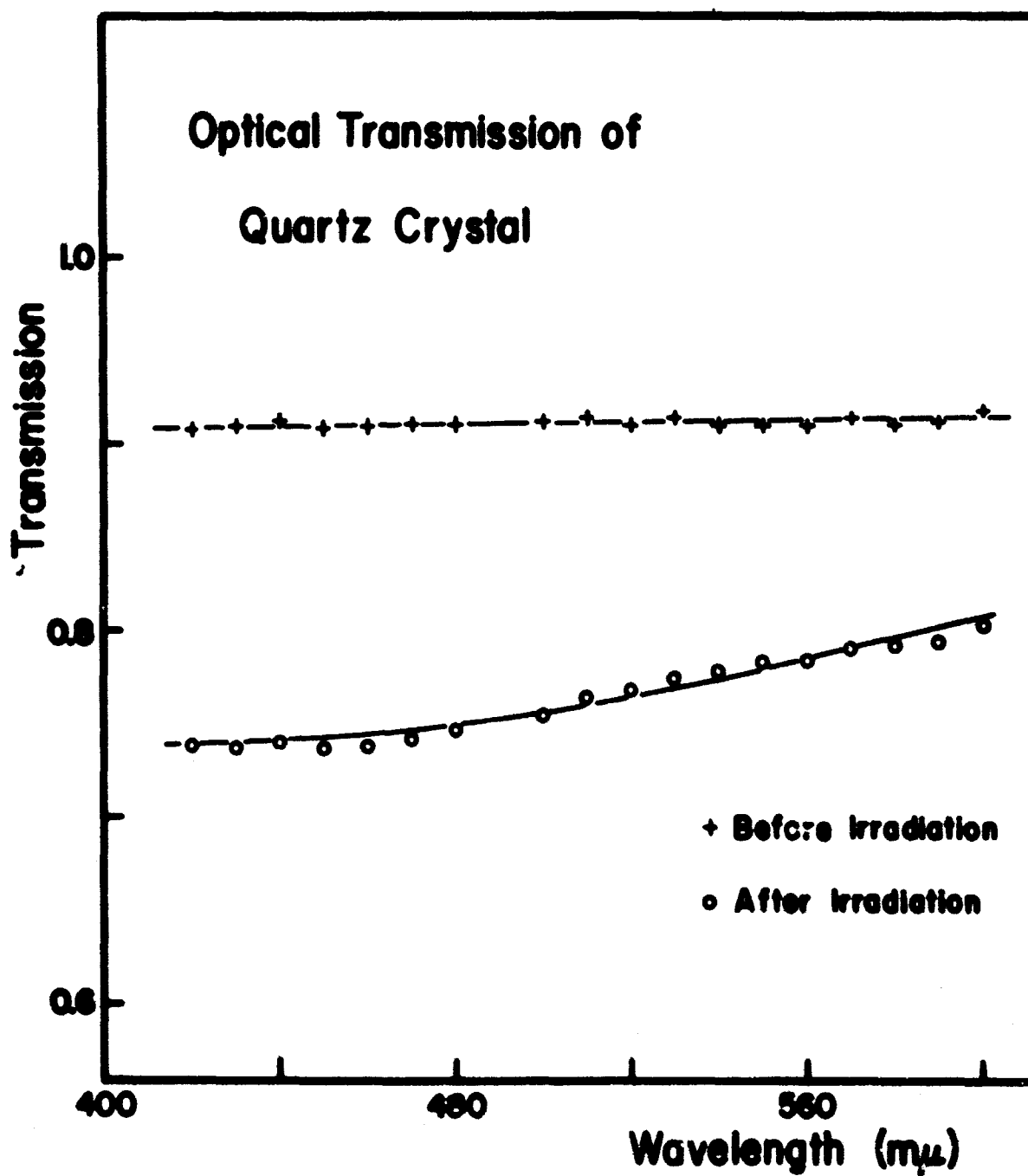After Irradiation

Fig. 5 - Optical Transmission of Irradiated Crystal
Before and After Irradiation

19

scatter. This scatter, which reduces the usefulness of the correlation, results from differences of shape of the single crystal diffraction patterns.

We consider, finally, the indices of asymmetry which have been calculated for each (1,-1) curve (see Tables I and II). The large scatter in these values indicates that there is no strong correlation with any of the other characteristics.

As has been stated previously, another characteristic of interest to us is the shape of the tails of the (1,-1) curve. In an attempt to establish a semiquantitative method of comparison of the tails, each (1,-1) curve was compared with a Lorentzian which was matched at the peak and half-maximum points. (The central region of such a curve is shown in Fig. 3.) Ratios of the (1,-1) curve ordinates to the Lorentzian ordinates at 5 and at 35 half-widths on either side of the peak were then calculated (see Table III). Note that the ratios for the etched crystals, except Y2, are less than one and those for the synthetic crystals are about the same as those for the natural crystals.

It is interesting to note that one crystal (YS-3-B3) displays an apparently anomalous behavior. Referring to Table II, it is seen that, even after 105 seconds of etching, this crystal has a (1,-1) width of 6.75 seconds when paired with Y4-F, and a reflection of 48.6 per cent. These results are, respectively, 38 per cent larger than and 24 per cent less than predicted. However, the measured coefficient of reflection, the tails of the (1,-1) curve, and the overlap factor and indices of asymmetry for the (1,+1) curve, as given in Table IV, are about the same as those of the other crystals. No explanation of this behavior is proposed.

Other apparent anomalies are involved in the measurements of w which are listed in Tables V and VI. For these measurements various crystals (YN-1-F, YN-1-B, YN-2-F, and YN-2-B) were paired first with Y4-F and then with Y3-F as the A crystal. We see that the value of w for YN-2-B and YN-1-B when paired with Y4-F is larger than the value of w for these crystals when paired with Y3-F. The reverse is true for YN-1-F and YN-2-F. Since Y3-F and Y4-F, when paired, give a symmetrical curve (see Table I) their diffraction patterns must either be identical or symmetrical, or both, as we shall see later. On this basis, then, one would expect that if w is larger for a given crystal when paired with Y4-F than when that crystal is paired with Y3-F, then w for any other crystal should be larger with Y4-F than with Y3-F. As we have seen, however, this is not necessarily the case. Two sets of values of w, measured at different times, are listed in Tables V and VI. Although the individual widths have changed somewhat,[18] the apparent anomaly which was pointed

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18. Y3-F and Y4-F when paired give, within experimental error, the same curves at both times, so we may infer that the change has occurred in YN-1-F, YN-2-F, and YN-2-B.

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out above is present in both sets of measurements. Although the reasons for the anomaly are not as yet understood, its existence points up the need for careful investigation of each pair of crystals.

Comparison with theory. The scattering of x-rays from crystals involves two main processes: coherent and incoherent scattering. No single theory to date takes simultaneous account of both types. On the one hand we have theories such as the Darwin-Ewald-Prins (DEP) theory which considers only coherent scattering from perfect crystals; and on the other hand we have separate theories for the various types of incoherent scattering, such as thermal diffuse scattering (TDS), Compton scattering, and scattering by imperfections in the crystal. The relative importance of the coherent and incoherent scattering varies with the part of the crystal diffraction pattern under consideration. In particular, the coherent scattering gives the major contribution in the central region around the Bragg peak, whereas the incoherent processes make their major contributions in the region of the tails of the crystal diffraction patterns. We shall therefore divide our discussion of the theories into two corresponding sections. We begin a discussion of the central region of the diffraction pattern with a consideration of the DEP theory.

The DEP theory assumes that[19]

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19. For a detailed discussion of the DEP theory see, e.g., R. W. James, Optical Principles of the Diffraction of X-Rays (G. Bell and Sons Ltd., London, 1950), Chap. II and the material of Appendix II of this thesis.

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1. All crystals have identical single crystal diffraction patterns.

2. Only Bragg reflection occurs, and the crystals are perfect.

Single crystal diffraction patterns (and from them (1,-1) and (1,+1) curves) have been calculated for calcite using the DEP theory,[20] but none

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20. A. H. Compton and S. K. Allison, X-Rays in Theory and Experiment (D. Van Nostrand and Co., New York, 1935), 2nd ed. p. 726.

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have as yet been calculated for quartz. The theoretical (1,-1) curve is obtained by plotting[21]

$$\phi(k) = \int_{-\infty}^{\infty} F_1(\ell)F_2(\ell-k)\,d\ell \quad ,$$

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21. For a discussion of this equation see Appendix II.

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where $F_1(\ell)$ and $F_2(\ell-k)$ are the diffraction patterns of the first and second crystals, respectively, and $\phi(k)$ is the ordinate of the (1,-1) curve when the angle between the crystals is given by k. If $\phi(k)$ is asymmetric, then F_1 and F_2 must be different and asymmetric functions. An examination of the indices of asymmetry given in Tables I and II shows that most of the curves are nearly symmetrical, and, for some, the assumption of identical diffraction patterns is probably good within a few per cent.

Other parameters of the peak region are w, P, and R. Values of these quantities have been calculated for quartz by Adell et al[22] and are listed in

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22. O. Adell, G. Brogren, and L. E. Haeggblom, Arkiv Fysik 7, 197 (1953).

Tables I and II. Comparing the experimental values of these parameters with

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those predicted by the theory, we see that for most of the crystals the agreement is within a few per cent. In the central region, then, the agreement between the theoretically predicted values of w, P, and R and the measured values of these quantities indicate that comparison with the theory can be used as a guide for determining the degree of perfection of crystals.

We now turn to the tails, and the incoherent scattering processes which are important in this region of the curve.

Chipman and Paskin[23] have studied the scattering of x-rays from lead

23. D. R. Chipman and A. Paskin, J. Appl. Phys. 30, 1992, 1998 (1959).

and copper in the region of Bragg peaks. They have concluded that for these materials the TDS can account for almost all of the tails of these peaks, and that the contribution to the integrated intensity may be as large as 15 per cent in the case of lead for Cu $K\alpha$ radiation. In addition, they point out that a calculation of TDS which takes account of two-phonon scattering processes exhibits peaks coinciding with some of the Bragg reflections and that occasionally these peaks are rather sharp. The role of the TDS in quartz has not been evaluated quantitatively and the results of Chipman and Paskin cannot be easily extrapolated to quartz because of the difference in the crystal structure. But, since the Debye temperature of quartz (about $500^{\circ}K$)[24] is much higher than that of lead (about $80^{\circ}K$), it is expected that

24. D. W. Berreman and T. T. Chang, J. Appl. Phys. 30, 963 (1959).

the TDS intensity would be much smaller for quartz. It would be of interest, however, to have calculations on the TDS in quartz because, to the extent that it is important in the central region, and particularly if it peaks at the Bragg peak, it will affect the shapes of the rocking curves and will need to be taken into account.

Compton scattering also contributes to the diffuse scattering in quartz. To the author's knowledge, no experimental information on the magnitude of this contribution is available and no calculations of it have been made. Such calculations would have to consider not only the effects of electron binding in the atoms, but also the fact that the atoms are in a crystal lattice. The probability of a Compton scattering process, which gives rise to an electron of a specific energy, depends on the availability of an empty energy level to which the electron may go, which in turn depends on the electron energy band structure of the crystal. Walker[25] has illustrated this

25. C. B. Walker, Phys. Rev. 103, 558 (1956).

point well for the case of aluminum. In an insulator such as quartz, the ejected electron must have a minimum energy, viz., the energy of the band gap, in order for the scattering process to have an appreciable probability of taking place. The Compton scattering in diamond has been observed by Alexopoulos and Brogren,[26] who report a gap between the Bragg scattered

26. K. Alexopoulos and G. Brogren, Arkiv Fysik $\underline{6}$, 213 (1953).

radiation and the Compton scattered radiation approximately equal to the known electron energy band gap. To the author's knowledge, the band gap for quartz has been neither measured nor calculated, but it is reasonable to assume that it lies in the range of 5 to 10 ev. The minimum separation between the energy of the Bragg peak and the Compton scattering should also lie in this range. As has been noted, there are no quantitative data available on the Compton scattering from quartz, but it is probably of the same order or magnitude as the TDS.

A third factor contributing to the shape of the diffraction pattern is scattering by imperfections in the lattice. The imperfections may be chemical impurities or mechanical imperfections such as dislocations. The misorientations produced by dislocations will broaden the (1,-1) curves and will also produce diffuse scattering, which is especially important in the tail region. The density of dislocations in a crystal may be inferred from the observed etch pit densities. Kurtz, et al, have reported a direct correlation between etch pit densities and $\overline{1,-1}$ curve widths for germanium.[27]

27. A. D. Kurtz, S. A. Kulin, and B. L. Averbach, Phys. Rev. $\underline{101}$, 1285 (1956).

In an effort to see if such correlations exist for quartz, etch pit densities were determined for several crystals, and are listed in Table VII. The average density, excluding crystal Y2, was 5×10^5 cm^{-2} while for Y2 it was 30×10^5 cm^{-2}. If we compare the (1,-1) curve width of Y2 with that of the remaining crystals (see Tables I and II), we see that an increase of a factor of six in the etch pit density has no appreciable broadening effect on the observed (1,-1) curve. However, since the etch pits are indications of dislocations which produce misorientations of the atomic planes, the crystals are obviously less than perfect.

Although the width of the (1,-1) curve seems to show no functional dependence on the number of dislocations, the tails of the (1,-1) curve do seem, at least in a rough way, to be so affected. From Tables I, III, and VII we note that crystal Y2 has the highest etch pit density and has also the highest tails of those crystals observed. On the other hand, the width of Y2 is about the smallest measured. If the height of the tails is in fact due to a large dislocation density, one might expect that the width would also be large. We do not at present have any explanation for why this is not so.

Analytic representation of a (1,-1) curve. Often in correction procedures, as a matter of convenience, the (1,-1) curve is replaced by a Lorentzian. We will now examine the validity of such substitutions.

A typical (1,-1) curve (that for YS-2-F1 with Y4-F) which has been normalized to unit intensity at the peak, and plotted as a function of the half-width at half maximum intensity (β), is shown in Fig. 3. The curve is compared with a similarly normalized Lorentzian of the same half-width plotted on the same scale. It can be seen that whereas in the central region the fit is within experimental error, beyond one half-width on each side the (1,-1)

curve falls below the Lorentzian. It has been the author's experience that a (1,-1) curve will eventually rise above its matched Lorentzian. Therefore, the points at which these two curves cross over may be used as a means of comparison. These crossover points, for the natural crystals, are listed in Table III. Unfortunately, the presence of the seed crystal in each synthetic plate geometrically limits the study of the (1,-1) curve to a region within forty half-widths on either side of the peak, and in each case the crossover, if it exists, is beyond this region. Therefore, in place of a crossover point, the ratios of the ordinates of the (1,-1) curve to that of the matched Lorentzian at 5 and at 35 half-widths from the peak are used as a basis for comparison. These ratios are listed in Table III.

In the correction procedures we also need information about the area under the tails of the curves. For a Lorentzian, the ordinate at a distance of 40β from the peak is 6.25×10^{-4}, and the area out to this abscissa value accounts for 99 per cent of the total area of the Lorentzian. If we arbitrarily consider the region of the tails as beginning at 2β, then the area under the Lorentzian tails amounts to 29 per cent of the area out to 40β; whereas the corresponding area under the (1,-1) curve amounts to about 13 per cent of the (1,-1) curve area out to that point. The difference in these two areas indicates clearly that one cannot use a single Lorentzian to represent a (1,-1) curve over its entire range and that special treatment must be given to the tails.

Single crystal diffraction patterns. If, in spite of the discussion of the previous section, one assumes that single crystal patterns can be represented by Lorentzians, then by pairing crystals and measuring (1,-1) curve widths, one can determine the width of these Lorentzians and predict (1,-1) curve widths for other combinations. This is quite simply done since, if A and B are the single crystal Lorentzian widths, the (1,-1) curve will be a Lorentzian whose width, w_1, is given by

$$A + B = w_1 \; .$$

This means that if one uses three crystals, having Lorentzian single crystal diffraction patterns of widths A, B, and C, then by taking (1,-1) widths of combinations of these crystals, two at a time, one can solve the following equations for A, B, and C:

$$A + B = w_1$$

$$A + C = w_2$$

$$B + C = w_3$$

This has been done for three crystals (Y4-F, Y1-F, Y3-F) and the results are given in Table V.

Since the single crystal pattern width of Y4-F has been calculated by the above method, the single crystal widths (Lorentzian shape) of the remaining crystals could be calculated from the values of w given in Tables I and II. With these numbers the values of w for several crystals in combination with Y3-F were predicted and then compared with experiments. The results of this are shown in Table VI. Although for the borad (1,-1) curves this method is not very accurate, it becomes more accurate as the (1,-1) curves become narrower.

Irradiation Effect

Various investigators have reported that crystals used in x-ray spectrometers show a definite deterioration of their x-ray reflection characteristics with time.[28] It seems reasonable to assume that these changes result

28. See R. Kvarda, M. S. thesis, The Ohio State University, 1957; R. J. Liefeld, Ph. D. dissertation, The Ohio State University, 1959; and J. O. Porteus, Ph. D. dissertation, Cornell University, 1958.

from a combination of surface corrosion and radiation damage. In fact, it has been observed that etching, or, in extreme cases, grinding and repolishing the crystals may restore the reflection characteristics to their original values.

In an attempt to study the relative importance of radiation damage in the deterioration process, one of the natural quartz crystals (Y1-F) was subjected to a dose of 5×10^6 roentgens of x-radiation from a Machlett AEG-50 copper target x-ray tube.[29] This dose was sufficient to produce a light tan

29. The x-ray tube was operated in a Picker diffraction unit, self rectified, at 30 PKV and 15 ma. The crystal was placed at a distance of 10 cm from the target and in such a position that the entire irradiated area received at least 90 per cent of the full beam intensity at that distance. A check of the optical transmission in the irradiated area showed it to be constant within ± 0.5 per cent

coloration in the irradiated area, and was probably more than a crystal would receive during an extended length of time in normal spectrometer use.

Before and after the crystal was irradiated, (1,-1) curves and measurements of per cent reflection were taken. The values of w, P, and R, and the Lorentzian crossover points are given in Table VIII and the (1,-1) curves are shown in Fig. 4. It is apparent that no appreciable change occurred on irradiation, indicating that, at least for this crystal, any change in the spectrometric properties resulting from the radiation damage is small and insufficient to explain the very much larger changes which other investigators have reported.

After the irradiation of crystal Y1-F, its optical transmission was remeasured as a function of wavelength. The results of this measurement, along with the transmission before irradiation, are shown in Fig. 5. The change in optical transmission on irradiation has been studied by Forman, who attributes

it to absorption by electrons trapped in F-center-like traps.[30]   It has

30.   G. Forman, J. Opt. Soc. Am. 41, 377 (1951).

recently been suggested, on the basis of nuclear magnetic resonance measure-
ments,[31] that the electrons trapped in these color centers have been removed

31.   J. H. E. Griffiths, J. Owen, and I. M. Ward in Report on the Conference
on Defects in Crystalline Solids, (The Physical Society, London, 1955), p. 81.

from Al⁻ ions which are substitutional replacements for Si atoms in the quartz
lattice.[32]

32.   The suggestion that the coloration of quartz is due to the presence of
Al⁻ ions is supported by the work of A. J. Cohen and H. L. Smith, J. Chem.
Phys. 28, 401 (1958), which reports a direct dependence of the color density
on the amount of aluminum present.

Since the irradiation induces only small shifts in electron densities
in the quartz, one should not expect a large immediate effect on the x-ray
reflection characteristics.[33]   It is quite possible that these displaced

33.   M. Wittels and F. A. Scherrill, Phys. Rev. 93, 1117 (1954), have shown
that bombardment of quartz with a high flux density of fast neutrons can com-
pletely destroy the crystalline structure. Such a result is not expected
from x-ray irradiation.

electrons act as catalytic agents for the surface corrosion, which in turn
produces the deterioration effect.

If this is indeed the case, then it seems likely that a crystal with no
aluminum, or other impurity content, and having a more nearly perfect lattice
from this standpoint, might deteriorate less rapidly.[34]   Of course these

34.   Crystals of higher purity and lower dislocation density than those in-
vestigated for this thesis are now being produced in the attempt to obtain
synthetic quartz of high "Q" for use as oscillators.   See J. C. King,
D. L. Wood, and D. M. Dodd, Phys. Rev. Letters 4, 500 (1960).

considerations are only speculation at present; one must also consider
physical defects such as dislocations when discussing lattice perfection.

CHAPTER IV

SUMMARY AND CONCLUSIONS

The results of this investigation show that synthetic quartz can be obtained with spectrometric properties which are sufficiently good to permit them to be used as replacements for natural quartz in high-resolution x-ray spectroscopy. It is possible that special high purity, high "Q", synthetic quartz mentioned in Chapter III may prove to be even better than any of the crystals, synthetic or natural, investigated for this thesis.

It has also been shown that a pair of crystals can be adequately characterized only by its complete rocking curve, and a comparison of these curves is the only reliable method of crystal selection. This has been pointed up by such apparent anomalies as two crystal pairs having the same (1,+1) curve width and different (1,-1) curve widths, and two crystal pairs having the same per cent reflection and different (1,-1) curve widths. The fact that the (1,-1) curve width for some crystal pairs changed in the relatively short time of five months indicates that if one widhes to make reliable resolving power corrections to observed spectra, he must keep a constant check on the shape of the (1,-1) curve.

The effect of x-radiation damage on the x-ray reflection characteristics of natural quartz has been investigated. It has been found that there are no immediate effects, although the displaced electrons may catalyze surface corrosion and thus may help to produce the long-term deterioration effects which have been observed.

APPENDIX I

RESOLVING POWER AND CRYSTAL DIFFRACTION PATTERNS

The resolving power of a spectrometer ordinarily refers to the ability of that instrument to separate two spectral lines so that they may be distinguished as such. The numerical resolving power of a spectrometer is defined as

$$R = \frac{\lambda}{\Delta\lambda} .$$

The question now arises as to what one should use for $\Delta\lambda$. In optics many criteria have been established,[35] while in two-crystal x-ray spectroscopy

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35. For a discussion of some of these criteria see R. W. Ditchburn, *Light* (Interscience Publishers, Inc., New York, 1953), Chap. 8.

$\Delta\lambda$ is taken as[36]

$$\Delta\lambda = \frac{d\theta}{D} ,$$

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36. A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment*, (D. Van Nostrand and Co., New York, 1935), 2nd ed., p. 712.

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where $d\theta$ is the angular width at half maximum intensity of the (1,+1) crystal diffraction pattern and the dispersion D is

$$D = \frac{2\tan\theta}{\lambda}$$

Since the (1,+1) diffraction pattern can be reasonably approximated by the (1,-1) curve, the value usually used for $d\theta$ is the width of the (1,-1) curve. In a larger sense, however, one is interested not only in the fact that a line is present in the spectrum, but also in the shape of the line. The numerical resolving power, while useful, does not provide sufficient information for the determination of the true line shape since the smearing of the incident spectrum depends on the shape of the crystal diffraction patterns; and a diffraction pattern with a narrow peak may have either low or high tails. Only if all diffraction patterns had the same shape, and that shape were known, would the numerical resolving power give complete characterization of a curve.

An observed spectrum $O(\nu_s)$ can be represented as the fold, or convolution, of the true incident spectrum $T(\nu)$ with the measuremental smearing function $M(\nu-\nu_s)$ of the spectrometer, i.e.,

$$O(\nu_s) = \int M(\nu-\nu_s)T(\nu)d\nu .$$

where ν_s is the spectrometer setting.[37] For a two-crystal x-ray spectrometer

37. For references to methods of solution of the convolution equation and the presentation of a new method of optimizing the solution, see J. O Porteus and L. G. Parratt, Technical Report No. 7 AFOSR TN 59-754, September 1, 1959.

the function $M(\nu - \nu_s)$ can be represented, at least in the region of the peak, by the (1,+1) diffraction pattern of the crystals. In the tail region other factors, such as slit geometry, must be taken into consideration. Also, since the (1,+1) diffraction patterns cannot at present be determined experimentally, the (1,-1) curve is used in its place.

The shape of the (1,-1) curve, and particularly the area under the tail relative to that under the peak, is important in determining the contribution of these two regions to the smearing. In fact, if a choice is to be made between two crystal pairs, one with low tails and a relatively wide peak, and one with high tails and a relatively narrow peak, the choice between them is not clearcut, and the situation must be examined closely to see which pair will produce the smaller smearing.

APPENDIX II

THE DARWIN-EWALD-PRINS THEORY OF X-RAY DIFFRACTION
FROM PERFECT CRYSTALS

This section contains a summary of the results of the DEP theory[38] and

38. For a more complete discussion of this theory see R. W. James, The Optical Principles of the Diffraction of X-Rays (G. Bell and Sons, Ltd., London, 1950).

a discussion of the precision with which values of the (1,-1) curve width, per cent reflection, and coefficient of reflection can be calculated from these results.

Single- and double-crystal diffraction patterns. Let $F(\ell)$ be the ratio of the intensity reflected from a crystal to that incident on it. Then[39]

$$F(\ell) = \frac{1}{2}\left|\frac{(A+iB)\ 1/\delta}{\ell-i(\beta/\delta)\pm\sqrt{[\ell-i(\beta/\delta)]^2-[(A+iB)/\delta]^2}}\right|^2$$
$$+ \frac{1}{2}\left|\frac{(A+iB)\ 1/\delta\ \cos2\theta_B}{\ell-i(\beta/\delta)\pm\sqrt{[\ell-i(\beta/\delta)]^2-[(A+iB)/\delta]^2\cos^2 2\theta_B}}\right|^2 \quad , \qquad (1)$$

39. The specific notation used here is that of G. Brogren, Arkiv Fysik 6, 321 (1953).

where

$$A+iB = \sum_i (F_i/Z_i)(\delta_i+i\beta_i) \quad ,$$

F_i = structure factor of the i-type atoms in the unit cell,

Z_i = total number of electrons associated with i-type atoms in the unit cell,

δ_i = unit decrement of the index of refraction of a material composed of i-type atoms,

$\beta_i = (\lambda/4\pi)\mu_i \quad ,$

μ_i = linear absorption coefficient of a material composed of i-type atoms,

$$\theta_B = \text{Bragg angle, and}$$

$$\ell = (\sin 2\theta_B/2)(\theta - \theta_B) - 1.$$

Equation (1) can also be written as

$$F(\ell) = 1/2\, F_\sigma(\ell) + 1/2 F_\pi(\ell) \quad , \tag{1a}$$

where $F_\sigma(\ell)$ refers to that part of the radiation whose electric vector is polarized perpendicular to the plane of incidence, and $F_\pi(\ell)$ to the radiation whose electric vector is parallel to the plane of incidence. Equation (1) is the equation of the single-crystal diffraction pattern as predicted by the DKP theory. If we assume that both crystals in a two-crystal spectrometer have the same diffraction pattern, the (1,-1) curve, and its width at half maximum, w, can be obtained by plotting

$$\phi(k) = 1/2 \int_{-\infty}^{\infty} F_\sigma(\ell) F_\sigma(\ell - k)\, d\ell + 1/2 \int_{-\infty}^{\infty} F_\pi(\ell) F_\pi(\ell - k)\, d\ell \tag{2}$$

for various values of k. With the same assumption, the coefficient of reflection and per cent reflection are given, respectively, by

$$R = \frac{2}{\sin 2\theta_B} \left\{ \frac{\left[\int_{-\infty}^{\infty} F_\sigma(\ell)\, d\ell\right]^2 + \left[\int_{-\infty}^{\infty} F_\pi(\ell)\, d\ell\right]^2}{\int_{-\infty}^{\infty} F_\sigma(\ell)\, d\ell + \int_{-\infty}^{\infty} F_\pi(\ell)\, d\ell} \right\} \tag{3}$$

and

$$P = \frac{\int_{-\infty}^{\infty} F_\sigma^2(\ell)\, d\ell + \int_{-\infty}^{\infty} F_\pi^2(\ell)\, d\ell}{\int_{-\infty}^{\infty} F_\sigma(\ell)\, d\ell + \int_{-\infty}^{\infty} F_\pi(\ell)\, d\ell} \quad . \tag{4}$$

These quantities have been calculated for the (10·0) planes of quartz at 1.537Å by Adell et al,[40] who give the following values:

40.   O. Adell, G. Brogren and L. E. Haeggblom, Arkiv Fysik 7, 197 (1953).

$$w = 4.9 \text{ sec,}$$

$$R = 1.82 \times 10^{-5} \text{ radians, and}$$

$$P = 64 \text{ per cent.}$$

In comparing experimental results with a theory such as the one discussed above, one should have some notion of the precision of the calculated results. Unfortunately, no statement of the precision is given by the above authors.

For calculations made using the DEP theory, probably the largest source of error lies in the values used for the atomic scattering factors. Other possible sources of error lie in the values used for the mass absorption coefficients and the unit decrement of the index of refraction. However, in the case considered here these errors are relatively small and will not be further discussed.

The atomic scattering factor[41] for a free atom at $0^{\circ}K$ is given by

41. For a more complete discussion of atomic scattering factors see Compton and Allison, op. cit., Chap. VI.

$$f_0 = \sum_{n=1}^{Z} \int u_n(r) \frac{\sin kr}{kr} dr \; , \qquad (5)$$

where Z is the atomic number, $u_n(r)\,dr$ is the probability that the n-th electron will be between the radii r and $r+dr$ from the center of the atom, and

$$k = \frac{4\pi}{\lambda} \sin 1/2 \; \phi. \qquad (6)$$

The values of f_0 used by Adell et al, are those given by James and Brindley,[42]

42. R. W. James and G. W. Brindley, Phil. Mag. 12, 81 (1931).

for which $u_n(r)dr$ was calculated by Hartree's self-consistent field method. There are no experimental values of f_0 for oxygen and silicon, but James and Firth[43] have measured values of f_0 for sodium and chlorine ions. A comparison

43. R. W. James and E. M. Firth, Proc. Roy. Soc. (London) A117, 62 (1927).

of theoretical and experimental values for sodium ions shows that the agreement is not better than about 3 per cent. This should be expected since atoms in a crystal lattice are different from the free atoms for which Eq. (5) is designed. It seems quite reasonable to assume then, that the predicted values of f_0 for silicon and oxygen at $0^{\circ}K$ are probably not accurate to better than about 3 per cent either.[44] Since Eq. (5) gives the scattering factor at

44. Atomic scattering factors for several elements have been calculated recently by A. J. Freeman, Acta Cryst. 12, 261 (1959), using more recent values of $u_n(r)\,dr$ than those used by James and Brindley. His results agree with those of James and Brindley at small values of $(\sin\theta)/\lambda$ but are about 3 to 8 per cent lower at large values.

$0^{\circ}K$, modifications due to temperature effects must now be taken into account.

It is well known that at a temperature T, the atoms in a lattice have a vibrational energy which is the sum of the zero-point energy and thermal energy. A theory for the effect of these vibrations on the atomic scattering

factors in a monatomic cubic lattice has been given by Debye and Waller.[45]

45. For a discussion of the Debye-Waller theory see R. W. James, op. cit., Chap. V.

In order to use the Debye-Waller theory, one must have a knowledge of the characteristic temperature of the material under consideration. In cubic crystals this characteristic temperature is a single number for a given material, but in crystals of lower symmetry, such as quartz, each principal axis of the crystal has a different characteristic temperature associated with it. Using an equation given by Post,[46] Berreman and Chang[47] have calculated these

46. E. J. Post, Can. J. Phys. 31, 112 (1953).

47. D. W. Berreman and T. T. Chang, J. Appl. Phys. 30, 963 (1959).

temperatures for quartz. If we substitute the characteristic temperatures given by Berreman and Chang into the Debye-Waller equation, we find that at $300^{\circ}K$

$$f = .985 \ f_o \text{ for oxygen and}$$

$$f = .991 \ f_o \text{ for silicon.}$$

Therefore, neglecting the temperature correction, as was done by Adell, et al, results in the use of scattering factors which are of the order of 1 to 2 per cent too large. However, since the actual values of f_o are probably not known to better than about 3 per cent, as indicated previously, neglect of the temperature correction is probably not serious.

In the foregoing discussion the necessity of a knowledge of the type of bonding in the crystal has not been mentioned. James and Brindley[42] have shown, however, that there is a considerable difference between the ionic and the atomic structure factors of an element. In the calculations of Adelle, et al, it was assumed that the bonding in quartz is wholly covalent, but as Glasstone[48] points out, it is believed that the bonding in quartz is about

48. S. Glasstone, Textbook of Physical Chemistry (D. Van Nostrand and Co., New York, 1946), 2nd ed., p. 390.

half ionic and half covalent. Neglect of the partial ionic character by not using an average of the atomic and ionic structure factors probably introduces an error of the order of 2 per cent.

Thus it can be seen that, because of the uncertainty in the values of the atomic scattering factors, the neglect of the temperature correction, and the assumption that quartz is a covalent crystal, the uncertainty introduced into the value of $F(l)$ is probably at least of the order of 2.5 per cent, and the calculated values of w, P, and R are probably known no better than

$$R = (1.82 \pm .05) \times 10^{-5} \text{ radians,}$$
$$w = 4.9 \pm .1 \text{ seconds, and}$$
$$P = 64 \pm 2 \text{ per cent.}$$

APPENDIX B

THE L X-RAY SPECTRA OF ELEMENTS IN THE SECOND TRANSITION GROUP

In addition to Zr, the work on which has been previously reported, investigations were conducted on the L emission spectra of Nb and Mo.

These elements share with Zr the problem of being refractory materials difficult to obtain in convenient high-purity forms. They also exhibit the same sensitivity to contamination by oxygen, nitrogen, and sulfur.

The data, presented as graphs of the spectra in the figures which follow, represent the best experimental results obtained thus far. While they represent well the qualitative aspects of the spectra, they are still to be considered preliminary. A detailed quantitative analysis and comparison with theory must await some additional data and the correction of the final experimental curves for various instrumental effects, and for the effects of finite inner state widths.
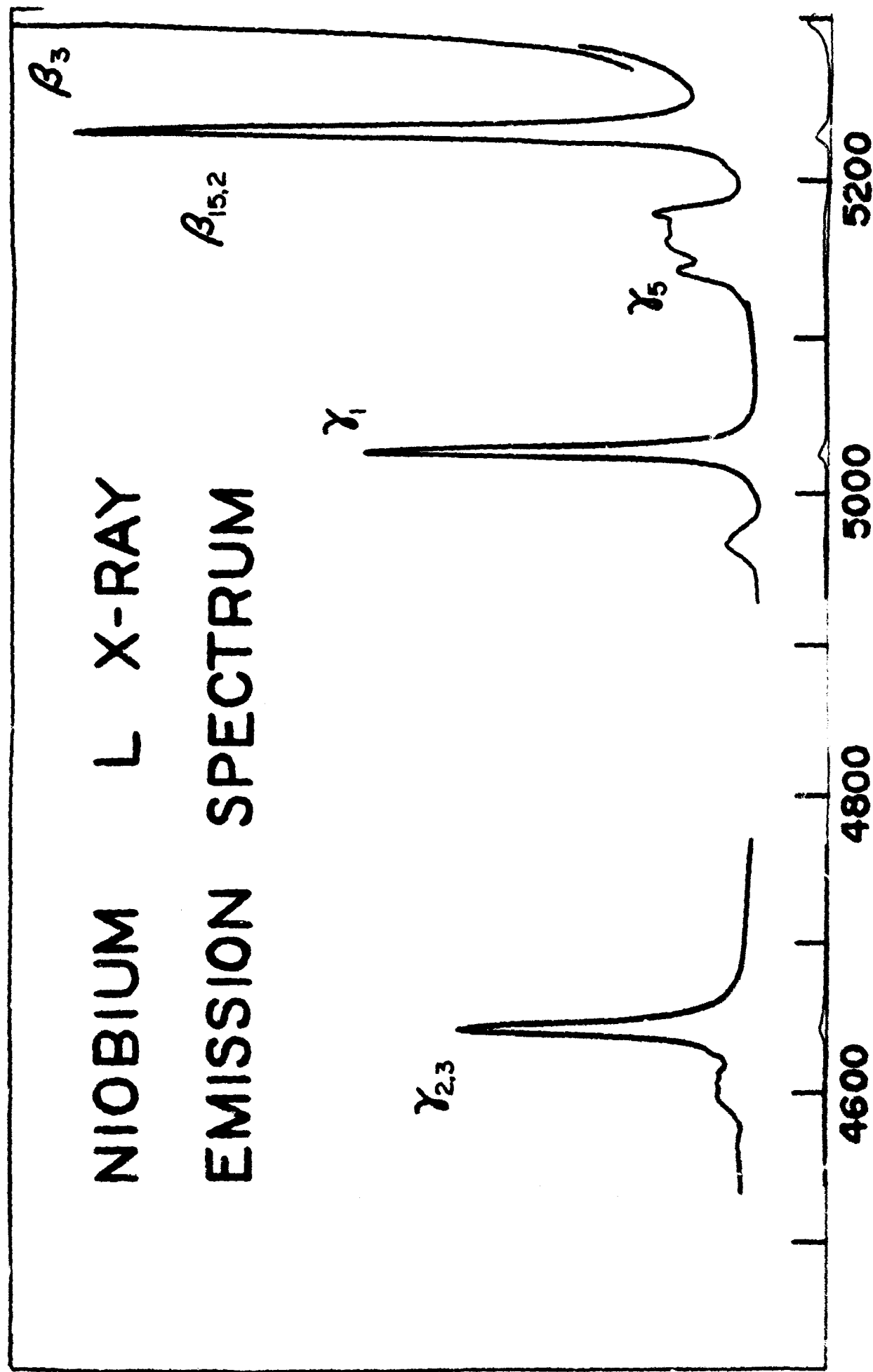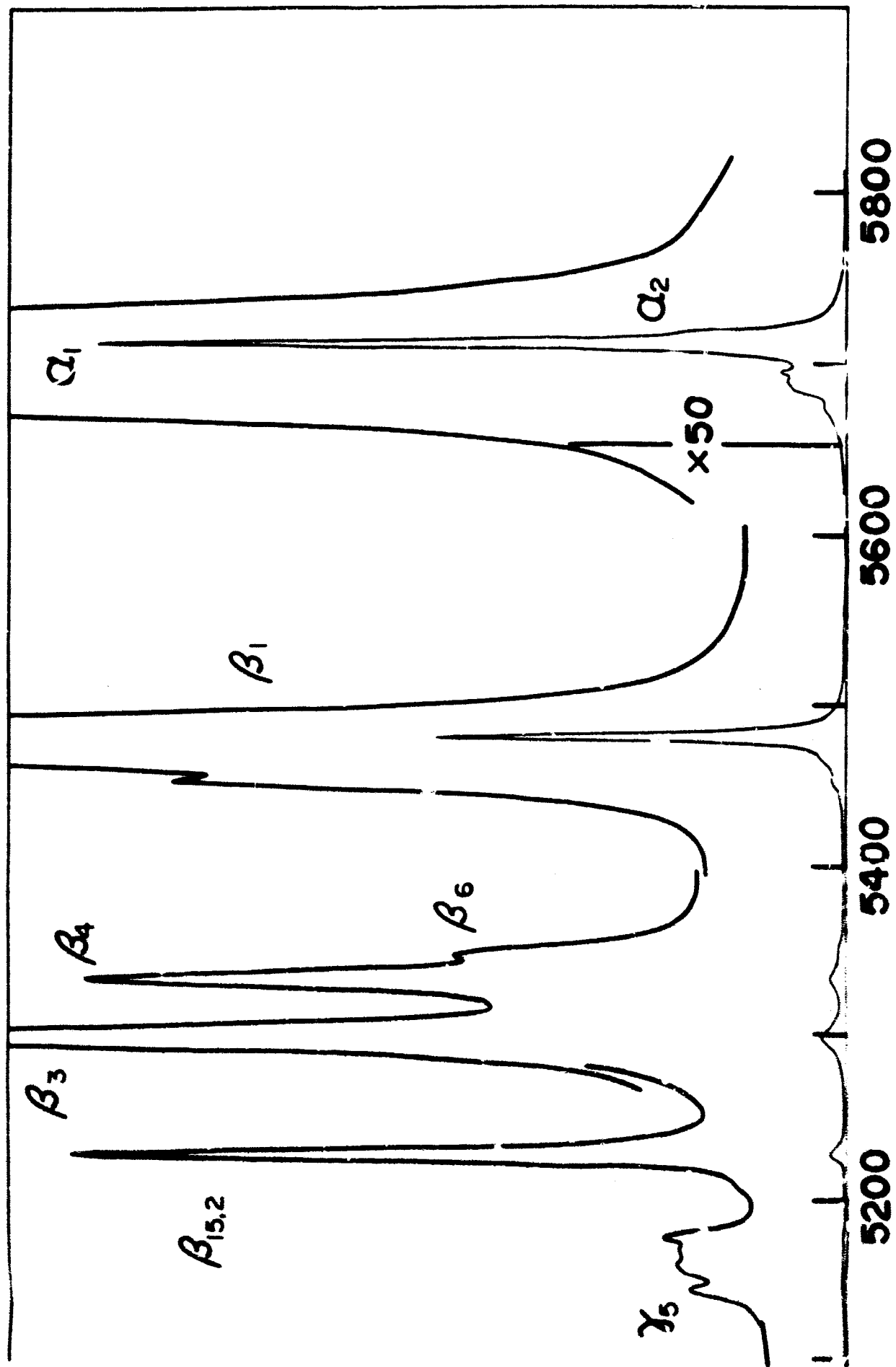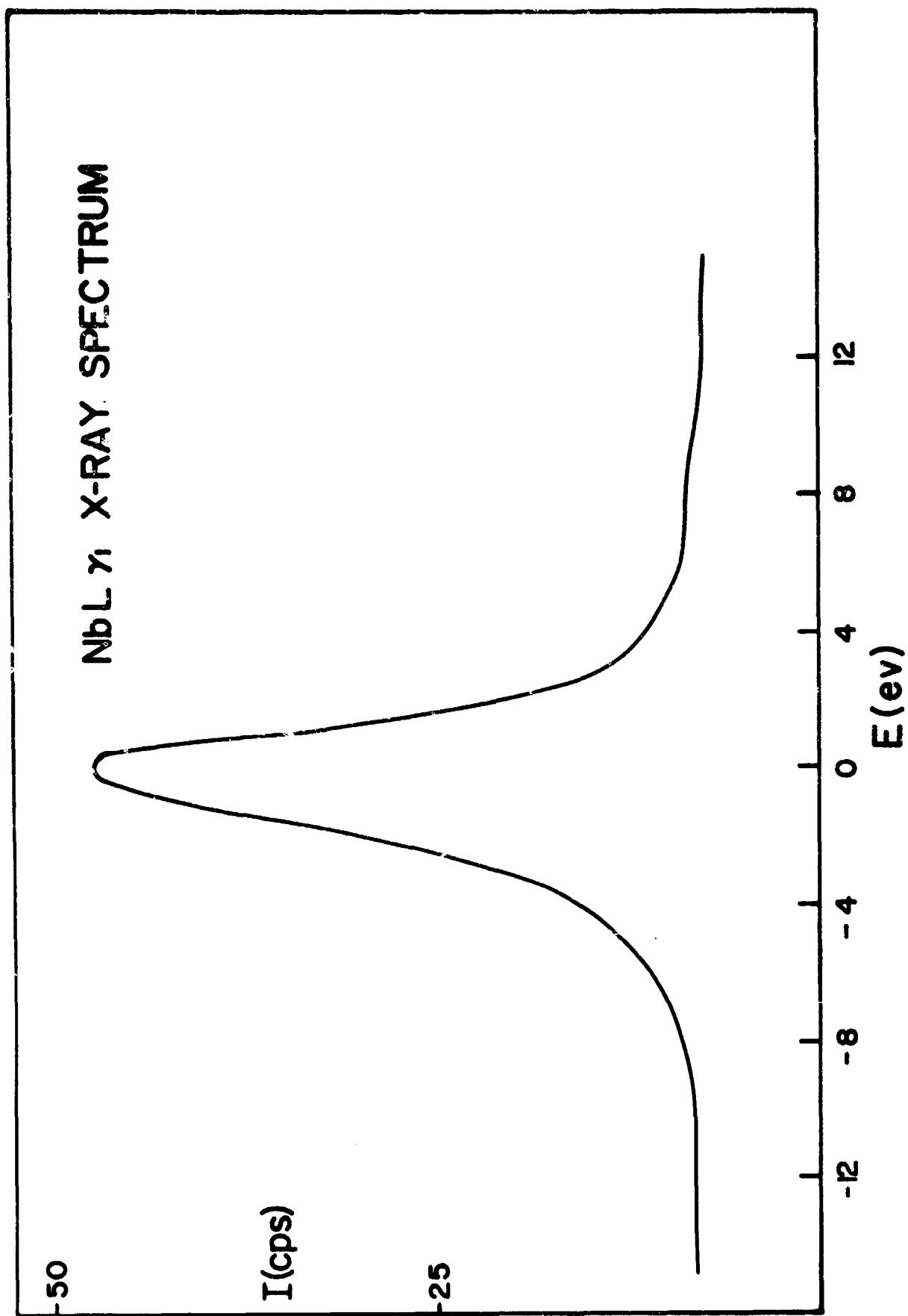
NIOBIUM L X-RAY EMISSION SPECTRUM

β_3 $\beta_{15,2}$ γ_5 γ_1 $\gamma_{2,3}$

4600 4800 5000 5200

Fig. 1

Fig. 1 - (continued)

NbL γ_1 X-RAY SPECTRUM

I(cps)

Fig. 2 – The Niobium L Emission Spectrum in the Neighborhood
of the γ_1 Band

Nb Lβ₂,β₃ X-RAY SPECTRUM

Fig. 3 - The Niobium L Emission Spectrum in the Neighborhood of the β₂ and β₃ Bands

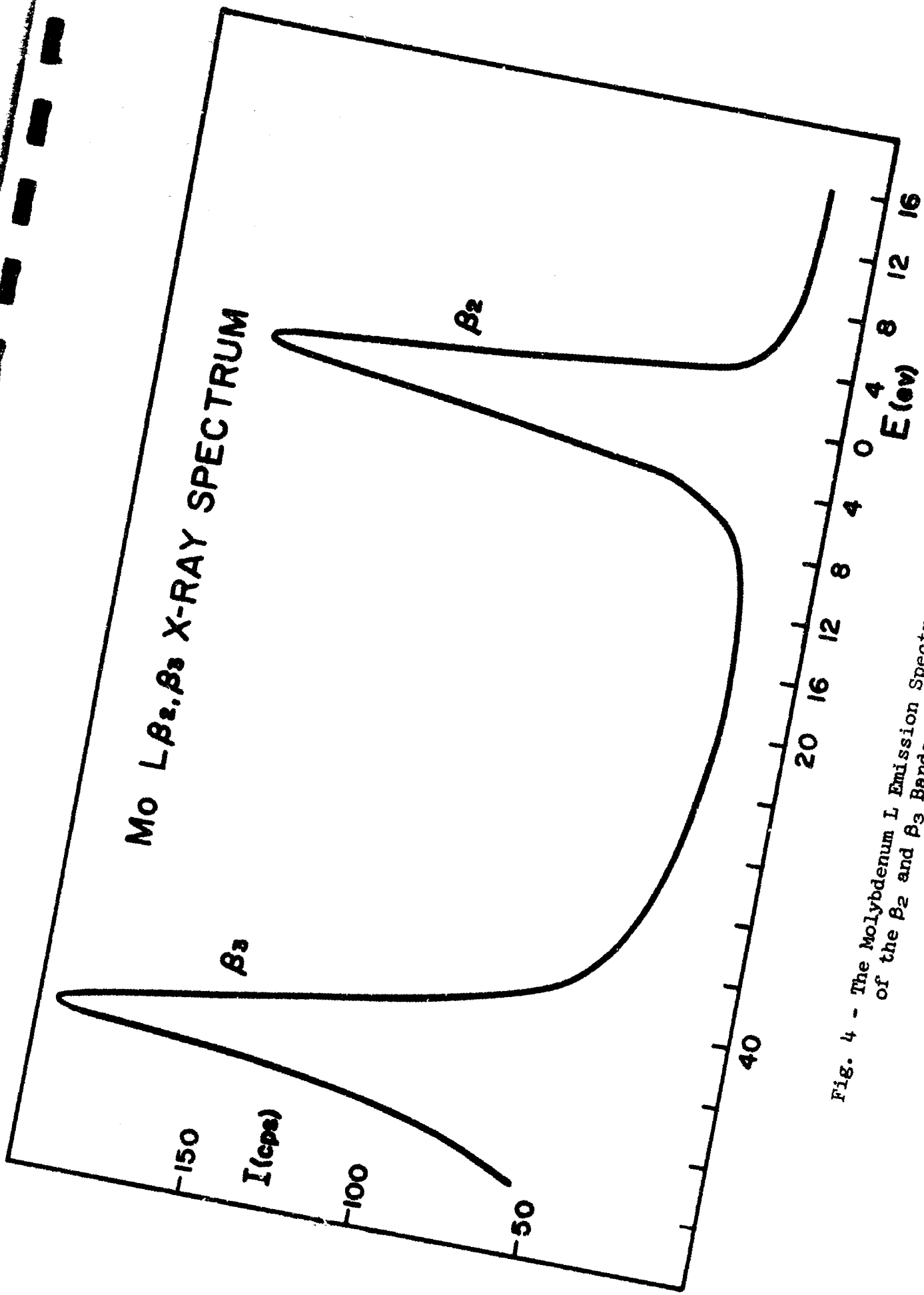Mo Lβ_2,β_3 X-RAY SPECTRUM
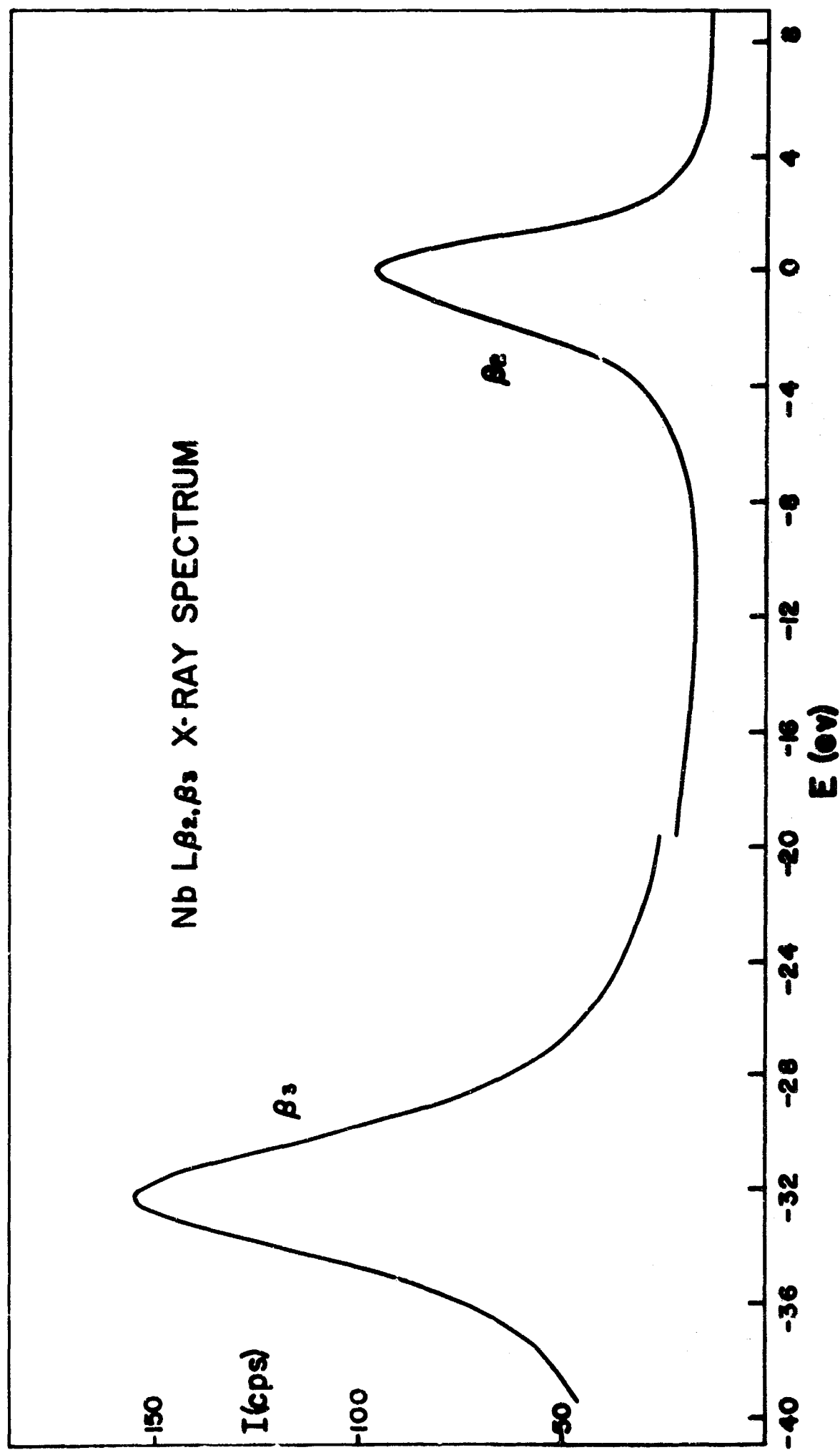
Fig. 4 - The Molybdenum L Emission Spectrum in the Neighborhood
of the β_2 and β_3 Bands

APPENDIX C

DESIGN CONSIDERATIONS FOR X-RAY SPECTROMETRIC INSTRUMENTS

Although two-crystal x-ray spectrometers have been in use for several decades, relatively little has been published on the details of their design. Discussion of the basic theory of the instrument by Schwarzschild, Schnopper's recent discussion of alignment and its effects on spectral measurement, and a handful of other papers constitute the available material in this area. The purpose of this note is to point out an effect which should be taken into account in spectrometer design and which has not, to our knowledge, been discussed elsewhere.

A common mode of operation of two-crystal spectrometers is that in which crystal A is held fixed in position and crystal B is rotated through some small angular range determined by the spectrometer geometry, x-ray beam walking, and the size of the crystals. Crystal A is then turned to a new position and the process repeated until the desired spectral region has been thus scanned. It is in this mode of operation that the effect with which we are concerned shows itself most clearly, though it is also present in the case in which the two crystals are rotated simultaneously.

The effect is most easily described as follows: Consider the case in which crystal A is fixed, crystal B is rotated, and the spectral region thereby examined contains a strong x-ray emission line and a much weaker line at some distance from it and near the edge of the allowable range of rotation of crystal B. When crystal A is now rotated so that the range of wavelengths Bragg reflected from it no longer includes the strong line, but does include the weaker (as a reference wavelength, say), a discrepancy appears in the measured intensities of wavelengths common to the two measurements.

This effect may be quite large, easily of the order of several per cent, and in extreme cases of the order of 50 per cent. One is thus in difficulty in trying to establish a coherent, precise, intensity scale over a long range of wavelengths in a spectrum. The effect arises from the fact that in the first case mentioned above the strong line is Bragg reflected from crystal A, whereas in the second case it is not. The scattering of radiation of this wavelength from crystal B is therefore very different in the two cases and accounts for the discrepancy in the intensity measurements. The amount of the discrepancy so produced depends on the relative intensities of the two spectral lines, on the physical diffraction patterns of the crystals (especially on the size and extent of the tail regions), and on the geometry of the spectrometer as it affects radiation scattered from the second crystal and seen by the detector.

While the effect cannot be avoided completely, proper attention in spectrometer design to the problems of collimation and of shielding against

scattered radiation can help to reduce its magnitude. Serious concern should be given to this problem whenever it is intended to use the spectrometer for precision measurements of relative intensities of spectral lines. The specific measures to be taken depend so much on the overall spectrometer design that they can not be discussed profitably as a separate issue.